

Stable Operation of Silicon-Based Anode for Lithium-Ion Batteries

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Project ID #: ES144



Overview

Timeline

- Project start date: Oct. 2016
- Project end date: Sep. 2019
- Percent complete: 25%

Barriers addressed

- Low energy density
- High cost
- Limited cycle life

Budget

- Total project funding
 - DOE share 100%
- Funding received in FY17: \$550k

Partners

- University of Pittsburgh (subcontract)
- General Motors

Relevance/Objectives

- Develop high-energy, long cycle life silicon (Si)-containing anode materials using low-cost synthesis approaches to replace graphite in Li-ion batteries.
- Improve the stability of solid electrolyte interphase (SEI) layer and materials interface to enable good cyclability.
- Develop innovative approaches to generate novel Si/C and Si/lightweight-inactive-matrix (LIM)-based anodes.
- Develop novel low-cost, viable, high energy mechanical milling (HEMM) and economical template-derived chemical and solution methods using cost-effective, environmentally benign and safe Si precursors.



Milestones

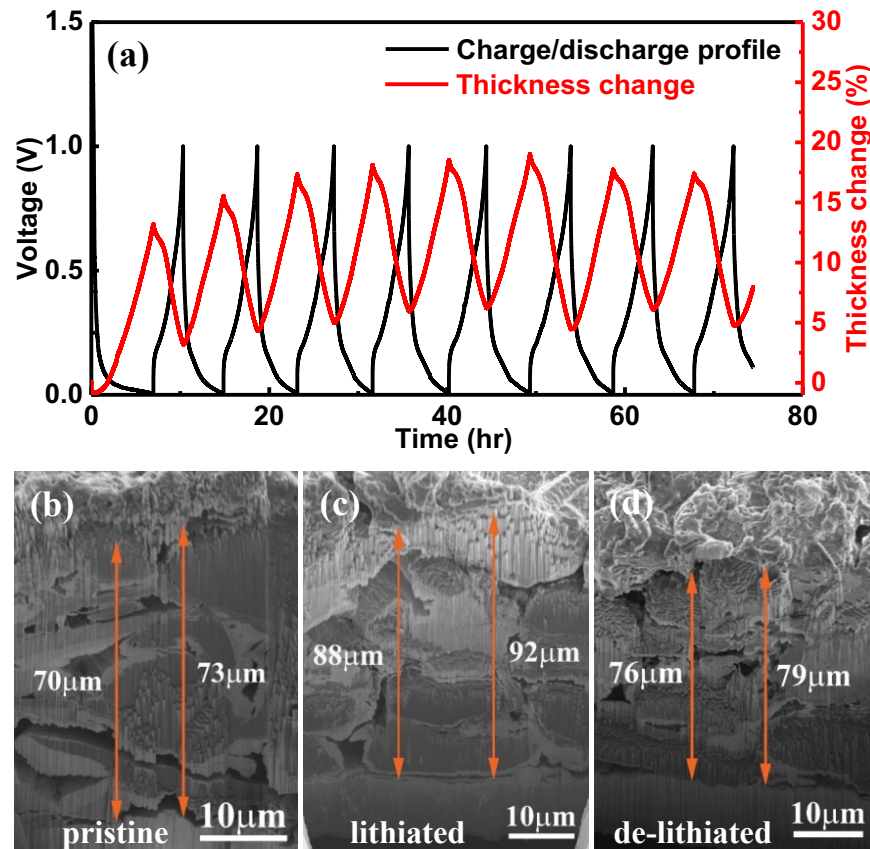
Date	Milestones and Go/No-Go Decisions	Status
Dec. 2016	Synthesize micron sized Si with the desired porosity and in situ grown graphene coating	Completed
March 2017	Synthesize low cost Si based nanocomposite anode materials using high energy mechanical milling (HEMM) and other economical template derived methods	Completed
June 2017	Identify new electrolyte additive to improve the stable operation of Si based anode.	Initiated 3/17
Sept. 2017	Fabricate and characterize Si based anode with desired electrode capacity ($\sim 3 \text{ mAh/cm}^2$)	To be started in 6/17

Approaches

- Develop micron-sized Si with nanoporosity and stable surface coating layer
 - Modify the thermite reaction method to prepare mesoporous Si from low cost precursors
 - Synthesize high-tap-density, high-capacity secondary Si particles of mSi-np using ultrasonic spray pyrolysis
 - Develop low cost approaches to coat artificial SEI layer on the surface of Si particles to enhance its cycling efficiency
- Synthesize Si-based nanocomposite anodes using high energy mechanical milling(HEMM) and other economical template-derived methods
 - Synthesize novel Si/C and Si/lightweight-inactive-matrix (LIM)-based anodes
- Investigate the alloying/dealloying mechanism and reaction kinetics and their impact on the solid electrolyte interphase (SEI) layers combined with the cycle life
- Design electrodes to achieve maximum loading and thickness by maintaining the targeted performance



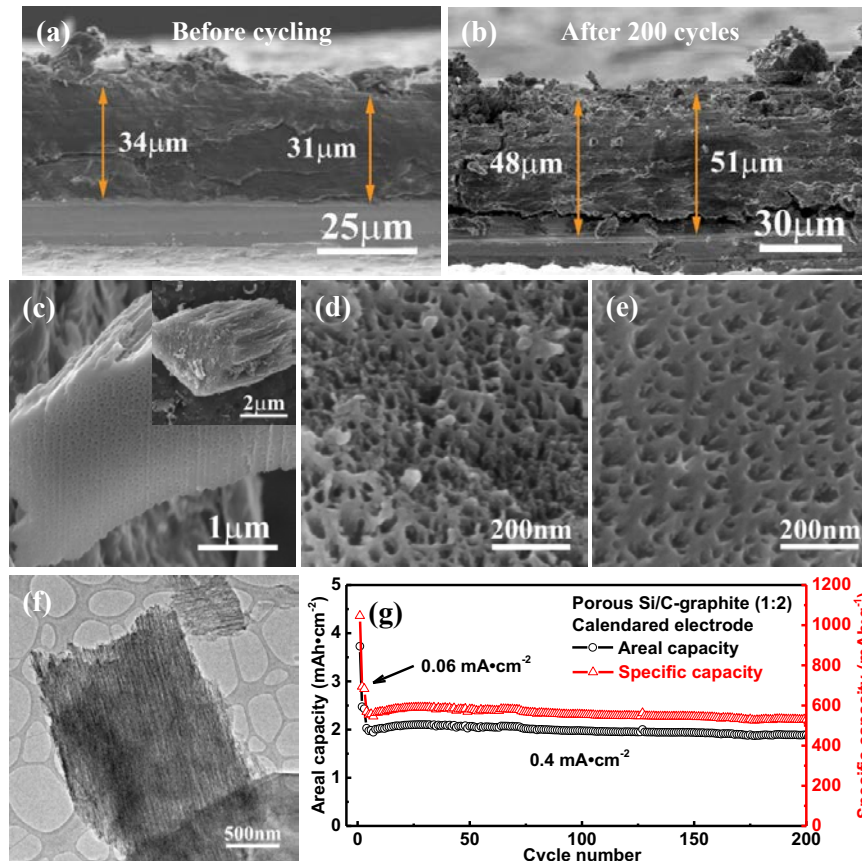
Technical Accomplishments and Progress - **Swelling of porous Si/C-graphite electrodes -**



- In-situ measurement using the electrochemical dilatometer (collaboration with General Motors) shows that the initial electrode swelling is $\sim 20\%$ after full lithiation and $\sim 7\%$ after de-lithiation.
- Ex-situ SEM study of the pristine electrode and cycled electrodes at charge and discharge states show that the electrode swelling at lithiated and de-lithiated state is 25% and $\sim 11\%$, respectively.

Technical Accomplishments and Progress

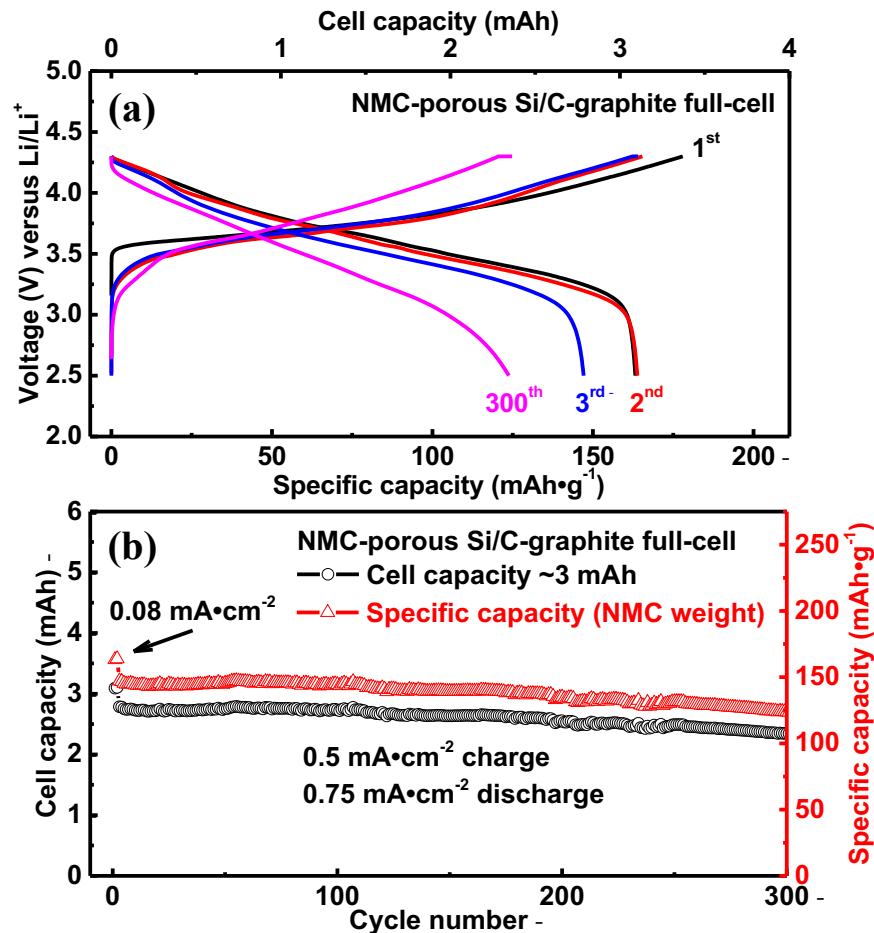
Calendering of porous Si/C-graphite electrodes



- The structure of the porous Si is largely maintained after electrode calendaring.
- The end-of-life swelling (200 cycles) of calendared electrode is $\sim 56\%$.
- The calendared electrode exhibits good cycling showing $>90\%$ capacity retention over 200 cycles.

Technical Accomplishments and Progress

NMC-porous Si/graphite full cell

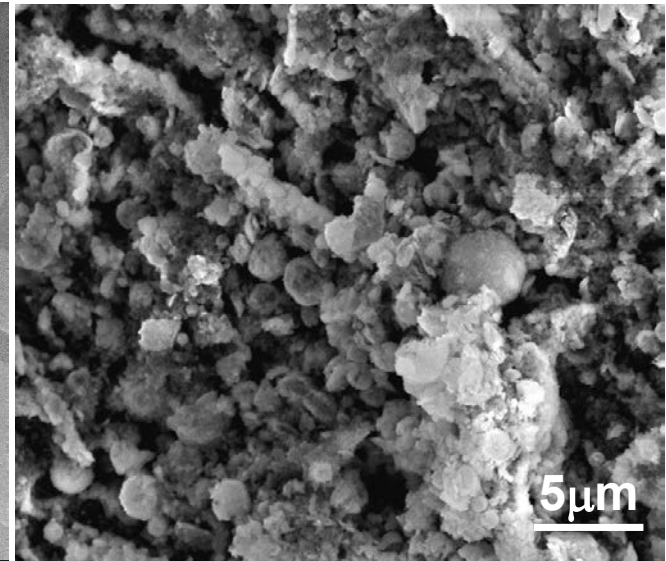
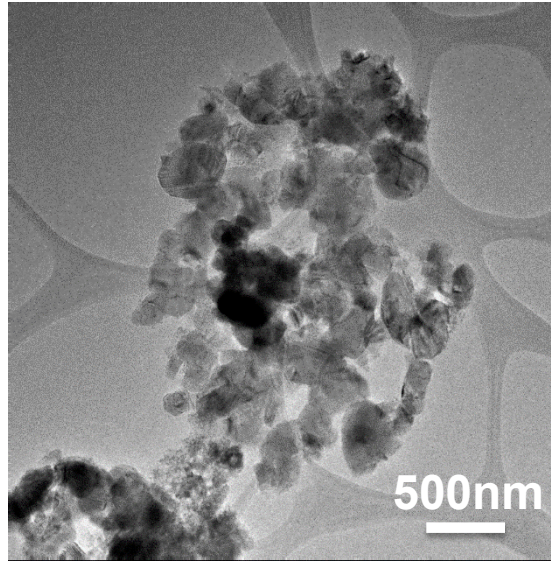
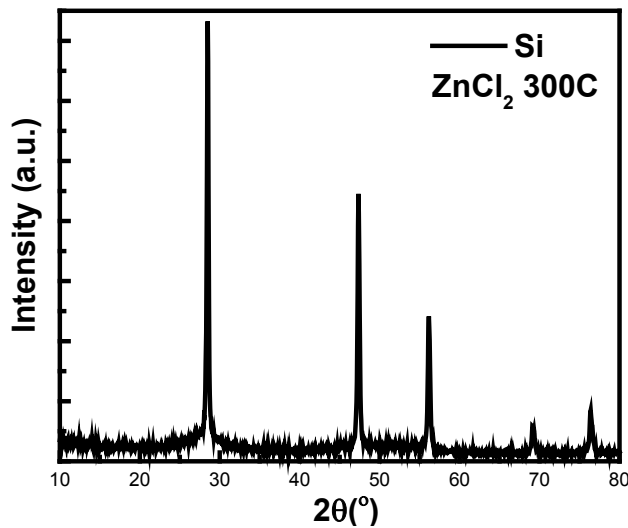


- The specific capacity based on NMC cathode (between 2.5 and 4.3V) is ~ 146 mAh/g, very close to the value (~ 150 mAh/g) obtained in NMC-Li half-cell.
- The full-cell shows good cycling stability with $\sim 84\%$ capacity retention over 300 cycles.

Technical Accomplishments and Progress

Low temperature thermite reaction

An example system:

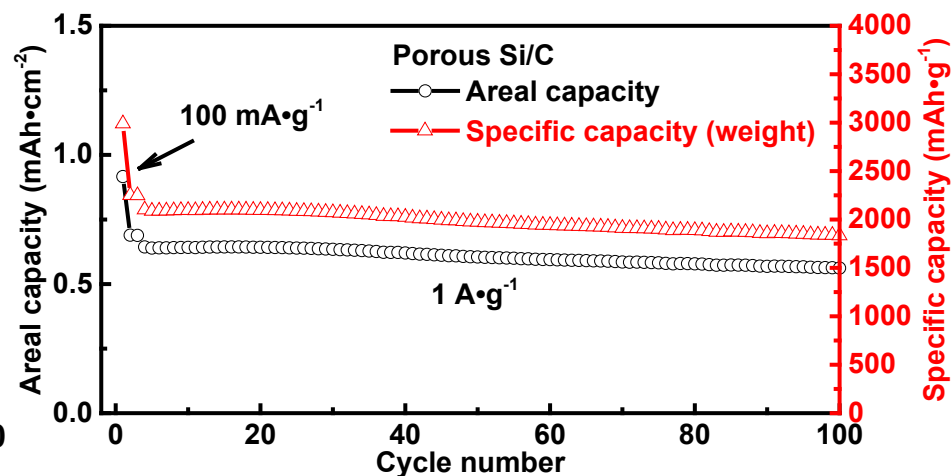
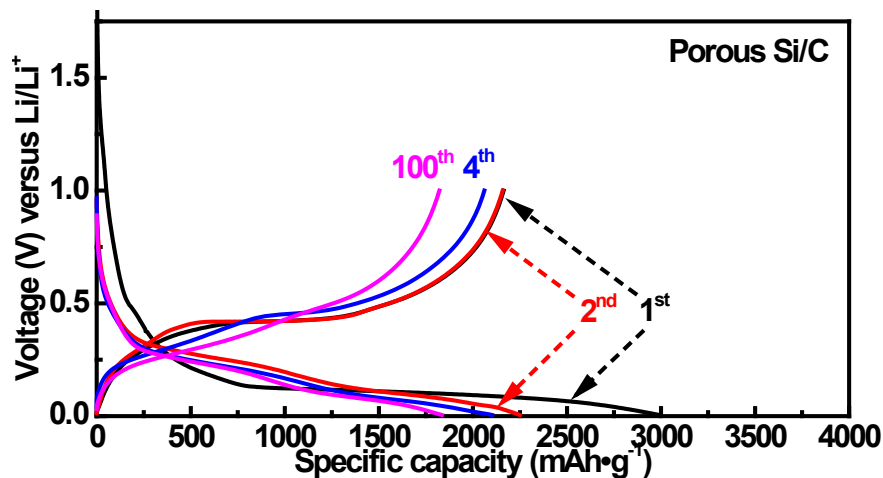


- A series of low temperature (300°C) thermite reactions have been developed to synthesize porous Si.
- Pure Si with the primary particle size of ~100 nm was obtained in the ZnCl₂ system.

Technical Accomplishments and Progress

Low temperature thermite reaction

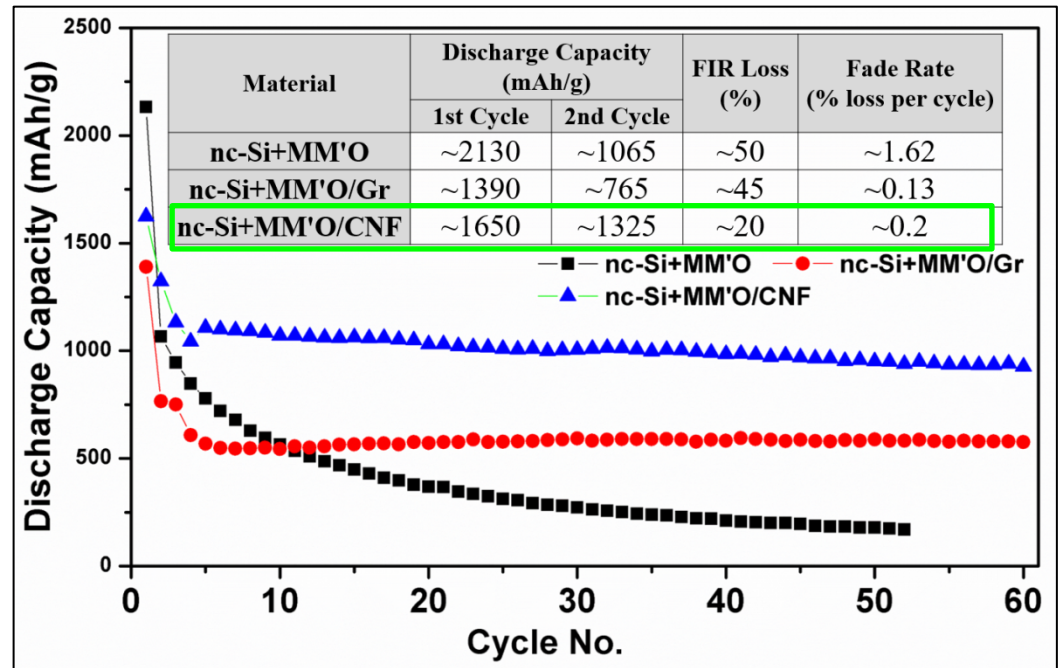
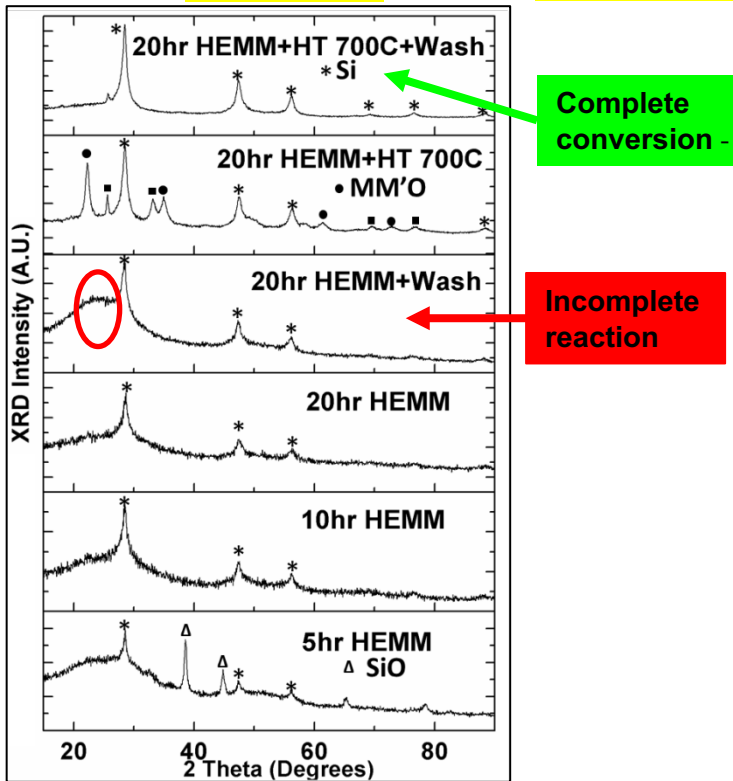
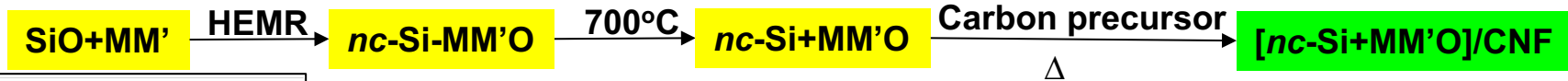
	BET surface area (m ² /g)	Pore volume (cc/g)	Pore size (nm)
Porous SiO ₂ (precursor)	100	0.98	30
Porous Si (product)	150.9	1.17	macropores



- The Si obtained inherits good porous structure from the SiO₂ precursor.
- The Si electrode has a specific capacity of ~2100 mAh/g at 1A/g current density and good cycling stability with ~86% retention over 100 cycles.

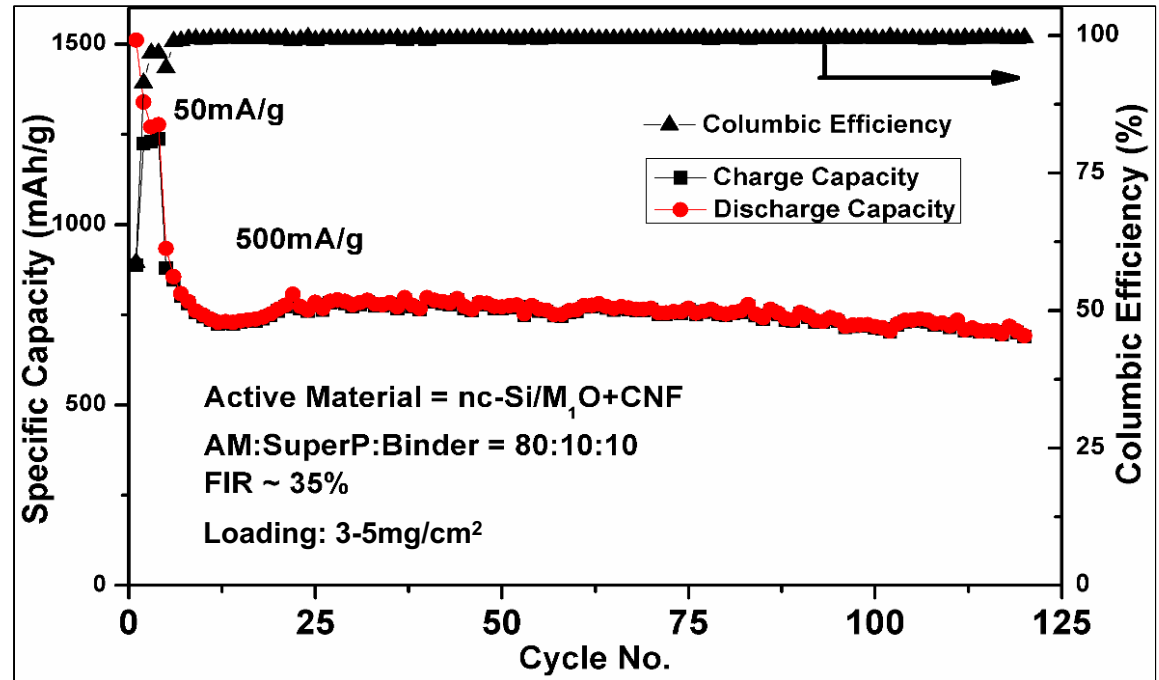
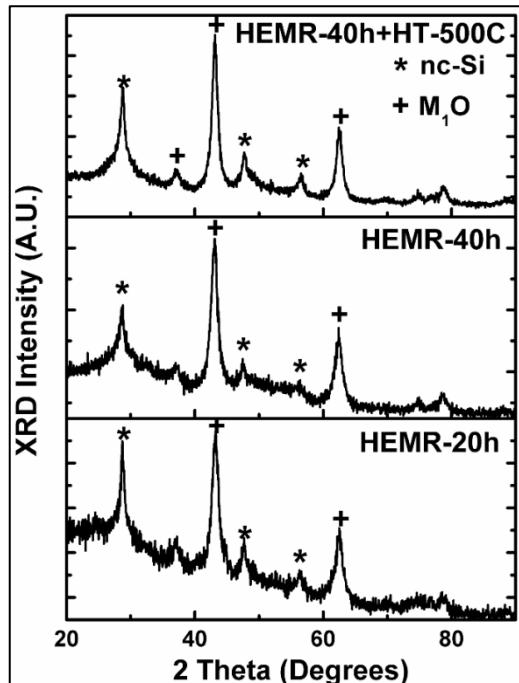
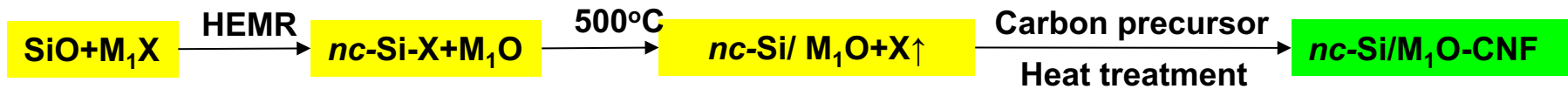
Technical Accomplishments

[*nc*-Si+MM'O]/CNF system



- The electrochemical performance of [*nc*-Si+MM'O]/CNF flexible fiber shows a 1st and 2nd cycle discharge capacity of ~1650 mAh/g and ~1325 mAh/g, respectively, with a FIR of ~20% and fade rate of ~0.13% loss/cycle.

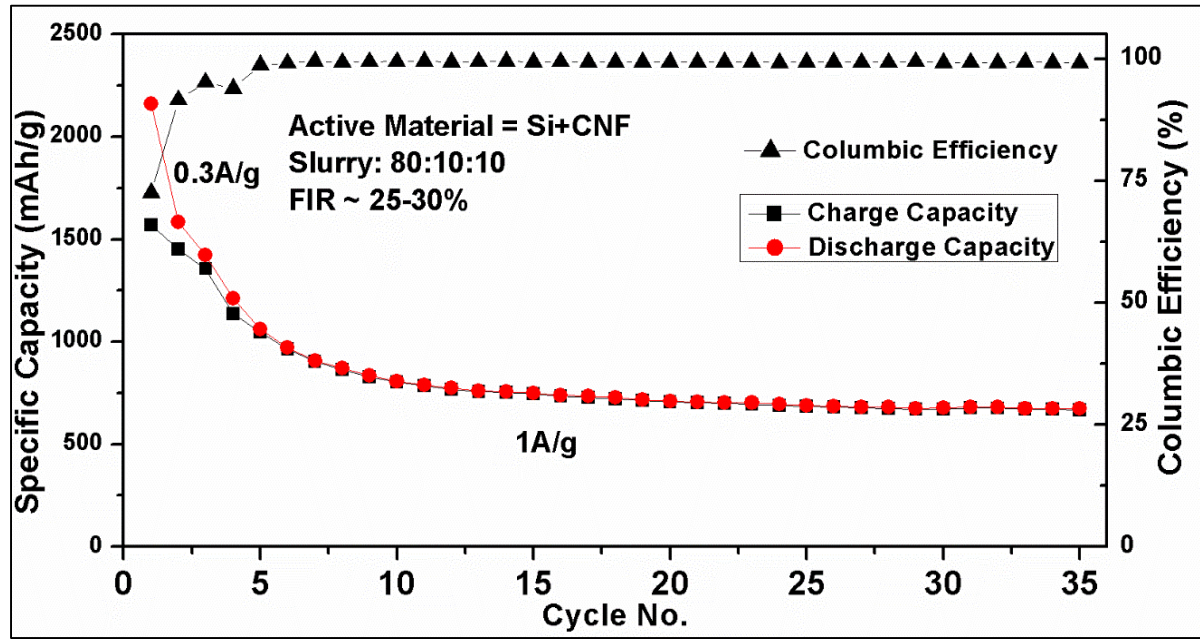
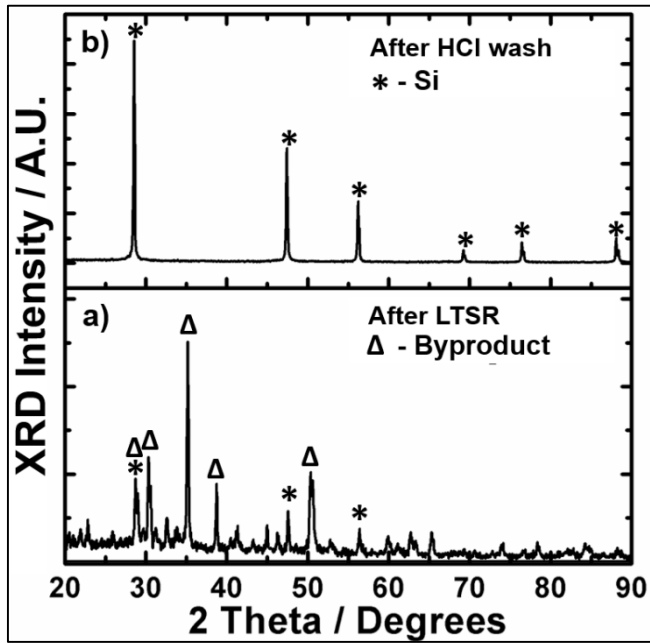
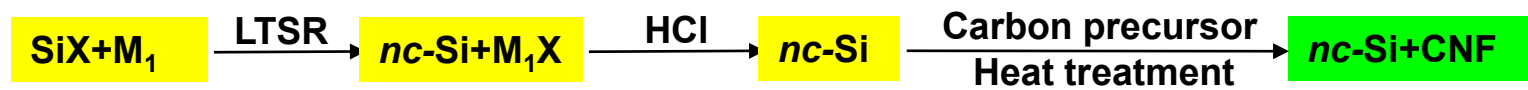
Technical Accomplishments - *nc*-nano Si/M₁O+CNF system -



- The *nc*-Si/M₁O+CNF system demonstrates a stable specific capacity of ~730mAh/g at the end of 120 cycles at a charge/discharge rate of ~0.5A/g with a columbic efficiency of ~99.65-99.82% and a fade rate of ~0.15% loss/cycle.

Technical Accomplishments

nc-nano Si+CNF system

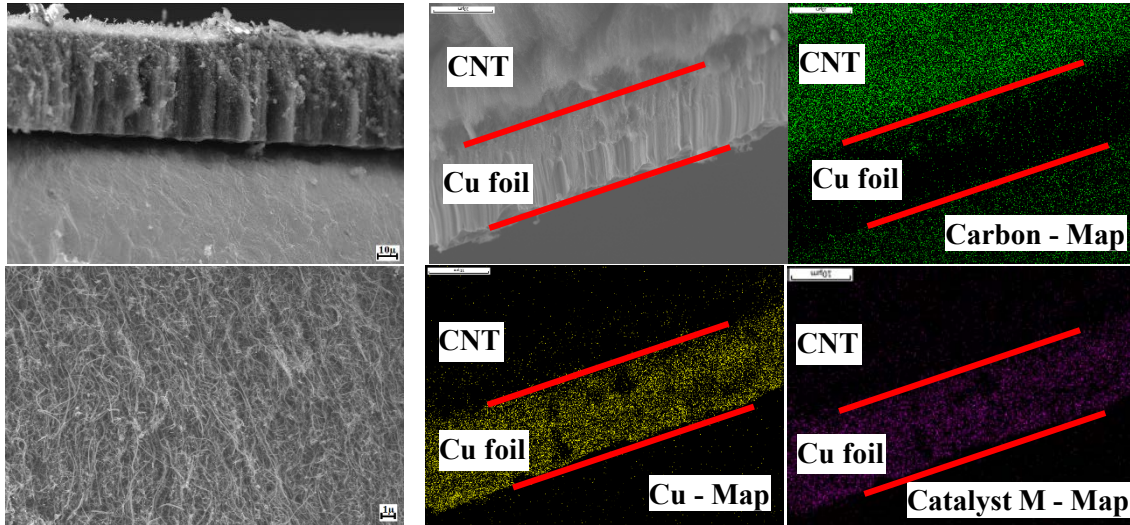


- XRD pattern shows evolution of *nc*-Si along with an inorganic byproduct obtained in the low temperature solid-state reduction (LTSR) approach.
- The Si/CNF material showed a first cycle discharge and charge capacity of ~2870mAh/g and ~2067mAh/g at a current rate of ~50mA/g, respectively, with an FIR loss of ~25-30%.

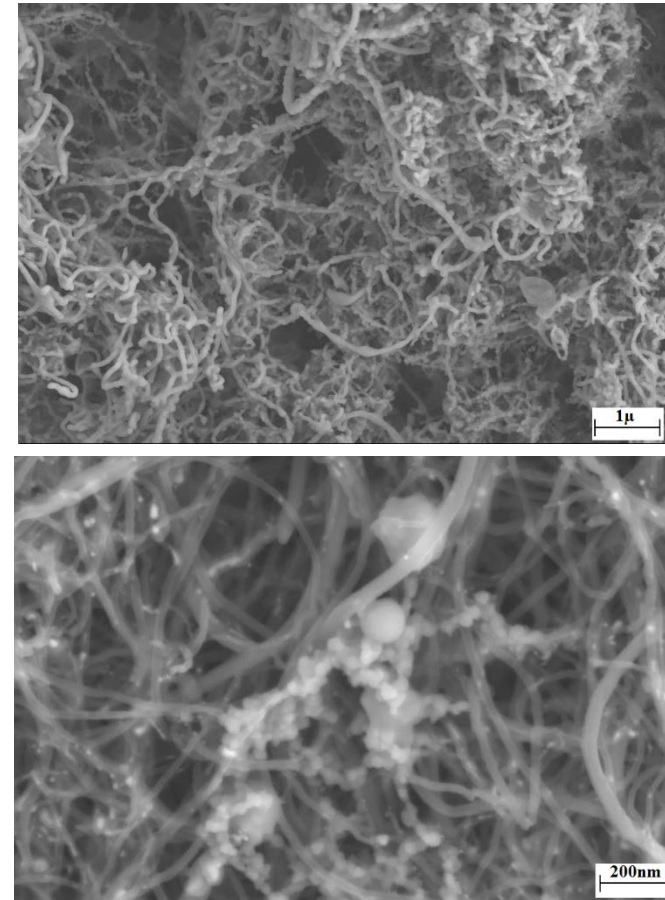
Technical Accomplishments

Binder less Electrodeposited (ED)Si/CNT system

High density MWCNT on Cu foil



Si/MWCT by electrodeposition



- Multi walled carbon nanotubes (MWCNTs) were grown directly on Cu foils.
- The thickness of the MWCNT layer is ~40-60 micron.
- Si was coated on these MWCNTs by electrodeposition from ionic electrolytes.
- SEM shows deposition of Si on the MWCNTs.
- Initial EDSi/CNT cycling study shows a 1st discharge capacity of ~2140mAh/g with an FIR loss of ~33-39%. Tests are on-going to evaluate long term performance in lithium-ion batteries as binder-less electrodes.

Responses to Previous Year Reviewers' Comments

- Project not reviewed in 2016

Collaboration and Coordination with Other Institutions

Partners:

- University of Pittsburgh (subcontract): Synthesis of Si-based nanocomposite using HEMM and other economical template-derived methods.
- General Motors: Collaboration on the in-situ measurement of electrode thickness change upon lithiation/delithiation.
- Stanford University: Study the failure mechanism of Si.
- Kurt J. Lesker Company, PA, USA
- Dr. Damodaran Krishnan Achary, University of Pittsburgh, PA
- Dr. A. Manivannan, Global Pragmatic Materials

Remaining Challenges/Barriers

- Identify and synthesize the active-inactive Si based nanocomposite with a specific capacity ~ 1000 mAh/g for full electrode with good cyclability.
- Develop interface control agents and surface electron conducting additives to reduce the first cycle irreversible loss and improve the Coulombic efficiency of Si based anode.
- Achieve stable capacity retention for thick electrodes (> 2 mAh/cm²) through optimization of the Si electrode structure and binder.
- Enhance the specific capacity of nc-Si/metal oxide/Graphite composite system derived from HEMR of SiO with alloys/metal reducing agents by inducing complete reduction.
- Develop new solution coating techniques to synthesize Si/C based nanostructured composites to improve the performance of the synthesized materials of nanoflakes and nanorods (NF and NR).

Proposed Future Work

- Identify and synthesize the active-inactive Si based nanocomposite with a specific capacity ~ 1000 mAh/g for full electrode with good cyclability.
- Further optimization of the thermite reactions to control the porous structure of the obtained Si and hence the electrochemical performance.
- Enhance the specific capacity and stability of nc-Si/CNF system by employing sacrificial coating to develop nc-Si/porous CNF.
- Develop new solution coating techniques to synthesize Si/C based nanostructured composites to improve the performance of the synthesized nanoflake (NF) and nanorod (NR) Si morphologies.
- Improve the loading density of the active Si material to achieve high areal capacity in the electrodes.
- Explore scalable and economic direct reduction especially using low temperature fluidized approach from cost effective precursors.

Any proposed future work is subject to change based on funding levels

Summary

- Stable operation of porous Si/C-graphite composite electrode with limited swelling has been demonstrate in both half cell and full cell designs.
- A series of low temperature thermite reactions have been developed to synthesize porous Si from porous SiO₂ precursor providing a potential low cost and scalable approach to porous Si with the desired porous structure and hence good electrochemical performance.
- [nc-Si+MM'O]/CNF flexible fiber shows improved first and second cycle discharge capacity of ~1650 mAh/g and ~1325 mAh/g, respectively, with a FIR of ~20% and a minimal fade in capacity (~0.13% loss per cycle).
- [nc-Si/M₁O+CNF] system shows a stable specific capacity of ~730mAh/g at the end of 120 cycles at a charge/discharge rate of ~0.5A/g with a columbic efficiency of ~99.65-99.82% and a fade rate of ~0.15% loss/cycle.
- Binderless *a*-Si/MWCNT on copper electrodes were developed using electrodeposition which show a first cycle specific capacity of ~2138 mAh/g at a current rate of 0.3A/g with an FIR loss of ~33-39%.

Acknowledgments

✓ Support from the DOE/OVT/BMR program is greatly appreciated

✓ Team Members:

PNNL: Xiaolin Li, Haiping Jia, Mishra Kuber, Sookyung Jeong,
Chongmin Wang, Pengfei Yan

Upitt: Prashant N. Kumta, Moni K. Datta, Bharat Gattu, Prashanth H.
Jampani

Technical Backup Slides



Publications and Presentations

1. X. L. Li, J. Liu, J.-G. Zhang, **Safe and low temperature thermite reaction systems and method to form porous silicon**. Patent application 23-97841-01.
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3. Liu B, J Zhang, and G Shen, **Pursuing two-dimensional nanomaterials for flexible lithium-ion batteries**. *Nano Today* 11(1):82-97. doi:10.1016/j.nantod.2016.02.003
4. X. L. Li, P. F. Yan, X. C. Xiao, J. H. Woo, C. M. Wang, J. Liu, J. -G. Zhang, **Design of Porous Si/C-Graphite Electrodes with Long Cycle Stability and Controlled Swelling**, submitted.
5. B. Gattu; Epur, Rigved; Jampani, Prashanth; Kuruba, Ramalinga; Datta, Moni; Kumta, Prashant, **“Silicon-Carbon Core-Shell (C@Si@C) Hollow Nanotubular Configuration - High Performance Lithium-Ion Anodes”**, Journal of Physical Chemistry – C (2017) in Press.
6. B. Gattu, P. H. Jampani, M. K. Datta, P. N. Kumta, “Water-soluble template derived nanoscale silicon nano-flakes and nano-rods morphologies: stable architectures for lithium-ion anodes”, *Nano Research* (2017) under review.
7. B. Gattu, R. Epur, P. Shanti, P. H. Jampani, R. Kuruba, M. K. Datta, A. Manivannan, P. N. Kumta, “Pulsed current electrodeposition of silicon thin film anodes for lithium-ion battery applications”, *Inorganics* (2017) under review.
8. B. Gattu, P. M. Shanthi, M. K. Datta, P. Jampani and P. N. Kumta, **“Synthesis of High Performance Si Nanoflakes and Nanorod Anode Morphologies Using Water Soluble Recyclable Templates for Lithium Ion Batteries”**, Conference Presentation, 229th ECS Meeting, May 29-June 2 2016, San Diego, CA.